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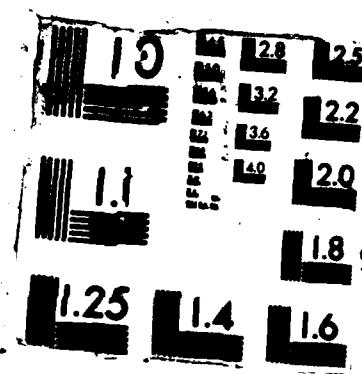
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Pentachloro(vinyloxy)cyclotriphosphazenes

by

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PENTACHLORO(VINYLOXY)CYCLOTRIPHOSPHAZENES

(2,2,4,4,6-Pentachloro-6-(ethoxy)-1,3,5,2λ⁵,4λ⁵,6λ⁵-triazatriphosphorine)

Submitted by Christopher W. Allen*, Kolikkara Ramachandran⁺ and
Douglas E. Brown*

Checked by

It has recently been found that the variety of new and useful phosphazene derivatives which are available can be expanded dramatically by incorporation of an organofunctional substituent on the phosphazene ring. The reactive center on the side chain can then serve as the site for further transformations in syntheses. This approach has been most successfully utilized with olefinic¹, p-lithiophenoxy², and p-aminophenoxy³ phosphazenes. One such class of organofunctional monomers is the vinyloxycyclophosphazenes which are available from the reaction of the enolate anion of acetaldehyde with halocyclophosphazenes.⁴⁻⁷ The lithium enolate of acetaldehyde is conveniently obtained by metalation of tetrahydrofuran⁸, and the reaction of this material with hexachlorocyclotriphosphazene results in the formation of pentachloro-(vinyloxy)cyclotriphosphazene, N₃P₃Cl₅OC₂H₃.⁴ This process is described below. The conversion of this monomer to polypentachloro(vinyloxy)cyclotriphosphazene is described in Sec. B.

A. PENTACHLORO(VINYLOXY)CYCLOTRIPHOSPHAZENE

(2-vinyloxy-2,4,4,6,6-pentachlorocyclotriphosphazatriene; 2,2,4,4,6-penta-chloro-6-(ethoxy)-1,3,5,2λ⁵, 4λ⁵,6λ⁵-triazaphosphorine



Procedure

The apparatus shown in the figure⁹ is fitted with a magnetic stirring

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bar, a 100-mL pressure-equalizing dropping funnel and septa on the two side arms. The glassware is assembled hot, the stopcocks are closed, and the system is flushed with nitrogen exiting through the dropping funnel to a mercury bubbler. The nitrogen flow is reduced to a minimal rate and 100-mL of dry tetrahydrofuran (THF) is placed in the apparatus. Using either a syringe or a double-ended needle, 50-mL of a 1.55M solution of butyllithium in hexanes (0.078 mole) is placed in the addition funnel and slowly added to the stirred THF. Stirring is continued overnight. A 500-mL three-necked flask is attached to the apparatus in the figure and is charged with 15.0g (0.043 mole)* of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$,[†] and a magnetic stirring bar. Septa are fitted to the side arms, and the flask is attached to the apparatus containing the lithium enolate. The nitrogen line is removed from the side arm on the apparatus shown in the figure and connected to the flask via a syringe needle. The upper stopcock of the apparatus is opened allowing the system to be flushed with nitrogen. Approximately 100-mL of dry THF is added to the flask, and stirred until the solid dissolves. The phosphazene containing flask is immersed in an ice bath and the enolate solution is slowly added. After complete addition, the stirred reaction mixture is allowed to warm to room temperature. The solvent is removed by means of a rotary evaporator, and the resulting oily mixture is treated with activated charcoal and 200-mL of low boiling (30-60°) petroleum ether. After filtration through celite or Filter-Aid, the solvent is removed and the process is repeated with 100-mL of petroleum ether and additional activated charcoal. After removal of the solvent an oily mixture remains. Flash chromatography¹⁰ is an efficient method of separating the monosubstituted derivative from materials with higher

*The high enolate/phosphazene ratio is used to ensure reaction of all of the $N_3P_3Cl_6$ which is difficult to separate completely from the desired product.

[†]Shin Nisso Kako Co., ltd. 3-1-60, Ukimai, Kita-ku, Tokyo, Japan 115.

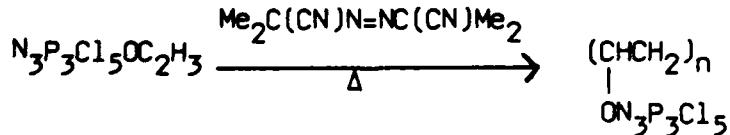
degrees of substitution. A 4 cm diameter chromatographic column fitted with a 35/20 ball joint at the top and leading to a nitrogen inlet is filled with 11cm of flash chromatography grade ($\sim 4\mu\text{m}$ average particle diameter) silica gel (Baker) in a slurry with low boiling petroleum ether. A 5.56-g sample of the crude product is placed on the column, solvent is added, the ball joint is clamped, and the nitrogen pressure is adjusted to provide a slow flow through the column. Fractions are collected in test tubes and monitored by thin layer chromatography. The first component to be eluted is the desired product, and all fractions containing this material are combined. The solvent is removed by means of rotary evaporation, kept at 40° . Purification is effected by short path distillation at a bath temperature of 85° (0.02 torr) to yield 2.25g of a water white liquid, bp $55-57^\circ$. Anal. Calcd. for $\text{N}_3\text{P}_3\text{Cl}_5\text{OC}_2\text{H}_3$: C, 6.75; H, 0.84; mol wt 353. Found: C, 6.74; H, 0.75; mol wt 353 (mass spectrum).

Properties

Pentachloro(vinyloxy)cyclotriphosphazene is a colorless liquid stable to atmospheric hydrolysis. It is soluble in common organic solvents. The infra red spectrum exhibits a strong phosphorus-nitrogen ring stretching band at 1220 cm^{-1} .⁴ The ^{31}P nmr spectrum shows resonances for $-\text{PCl}(\text{OC}_2\text{H}_3)$ centers at 13.2 ppm and $-\text{PCl}_2$ centers at 23.4 ppm with $^2J_{\text{PNP}} = 64\text{Hz}$.⁴

B. POLY[PENTACHLORO(VINYLOXY)CYCLOTRIPHOSPHAZENE]

(poly[(2-vinyloxy-2,4,4,6,6-pentachlorocyclotriphosphazene)], poly[1-[2,2,4,4,6-pentachloro-1,3,5,2 λ^5 ,4 λ^5 ,6 λ^5 -triaztriphosphorine]



Polymerization through the vinyl function in pentachloro(vinyloxy)cyclotriphosphazene can be accomplished under radical initiation conditions. The presence of moisture and (vinyloxy)phosphazenes with degrees of substitution

greater than one must be avoided in that the former can effect chain transfer and the latter results in the formation of cross-linked materials.

Procedure

A 2.25-g sample of pentachloro(vinyloxy)cyclotriphosphazene is distilled at 0.02 torr from P_4O_{10} to a flask containing 0.02g 2,2¹-azobis(2-methylpropane-nitrile) (azobis(isobutyronitrile)) (AIBN).** After distillation, the stopcock leading to the vacuum system is closed, and the flask (still attached to the distillation apparatus) is placed in a constant temperature bath at 60°. The flask is occasionally swirled to aid in dissolution of AIBN and to recover AIBN which condenses on the upper walls of the flask. The transition to a very viscous medium occurs in approximately two hours. At this point, the mixture is dissolved in 50-mL of dichloromethane and the resulting solution is dropped slowly down the wall of a 400-mL beaker containing 200-mL of stirred methanol. The polymer is allowed to settle, and most of the solvent is decanted. Approximately 200-mL of additional methanol is added and then decanted after the polymer has settled. The polymer is isolated by filtration through coarse filter paper, dried in an oven at 50°, and then placed in vacuo (0.02 torr) overnight. A yield of 0.27g (12% conversion) is obtained. Conversions of 10-20% are typically achieved with higher conversions being possible with extended reaction times. Anal. Calcd. for $N_3P_3Cl_5OC_2H_3$: C, 6.75; H, 0.84. Found: C, 7.16; H, 0.93.

Properties

Poly[pentachloro(vinyloxy)cyclotriphosphazene] is a white solid which is stable to atmospheric hydrolysis. It is soluble in toluene, dichloromethane etc., and can be cast into flexible thin films. Molecular weights will vary with experimental conditions with M_n as high as 2.85×10^6 (membrane osmometry) being observed. Thermal decomposition of the polymer is a complex process, with

**AIBN is purified by vacuum sublimation at ambient temperature.

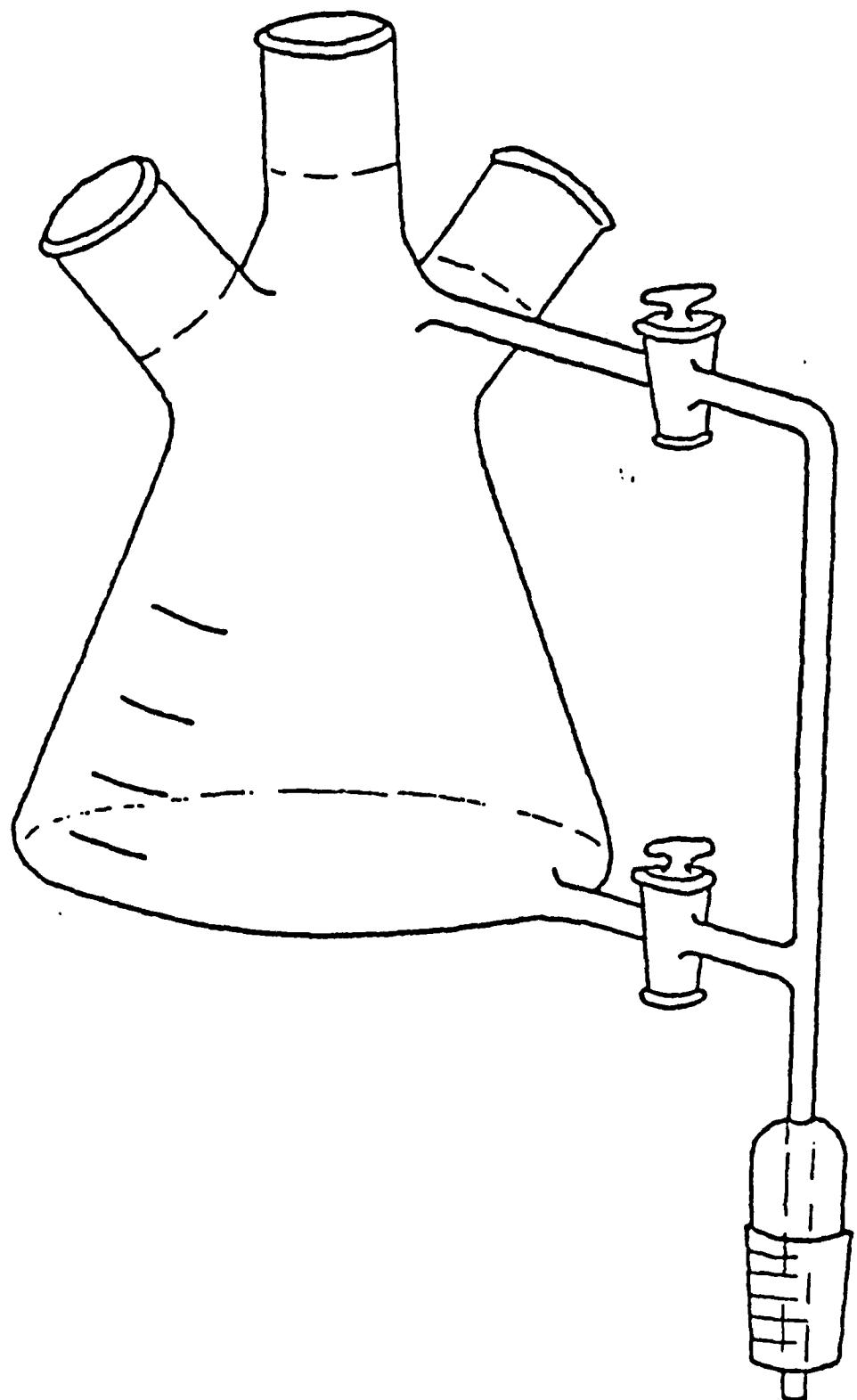
the first stage being elimination of HCl starting around 180°. Nucleophilic substitution reactions on the cyclophosphazene groups in the polymer allow for the synthesis of a broad range of related polymers.

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